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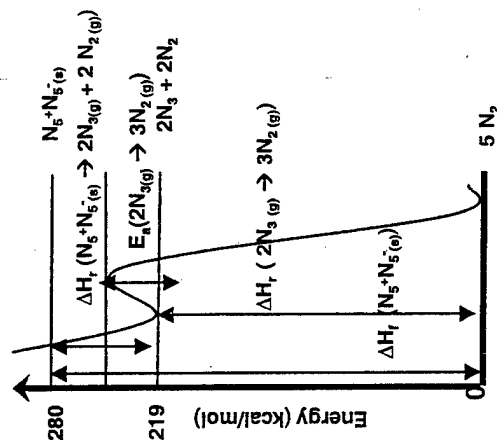
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$$\mathbf{N}_5^+\mathbf{N}_5^- \text{ and } \mathbf{N}_5^+\mathbf{N}_3^-$$

## POTENTIAL CANDIDATES FOR NITROGEN ALLOTROPES?

## CAN THEY EXIST?



**David A. Dixon,\* David Feller, Karl O. Christe,\***

**William W. Wilson, Ashwani Vij, Vandana Vij, H. Donald Brooke Jenkins,**

**Ryan M. Olson, and Mark S. Gordon**

# Enthalpies of Formation of Gas Phase $N_3$ , $N_3^-$ , $N_5^+$ , and $N_5^-$ from *Ab Initio* Molecular Orbital Theory, Stability Predictions for $N_5^+N_3^-$ and $N_5^+N_5^-$ , and Experimental Evidence for the Instability of $N_5^+N_3^-$

David A. Dixon,<sup>\*,†</sup> David Feller,<sup>†</sup> Karl O. Christe,<sup>\*,\*,#</sup> William W. Wilson,<sup>‡</sup> Ashwani Vij,<sup>‡</sup> Vandana Vij,<sup>‡</sup> H. Donald Brooke Jenkins,<sup>§</sup> Ryan M. Olson,<sup>††</sup> and Mark S. Gordon<sup>††</sup>

Contribution from the Chemical Sciences Division and Fundamental Sciences Division, William R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352, Air Force Research Laboratory, Edwards Air Force Base, California 93524, Loker Hydro-carbon Research Institute, University of Southern California, Los Angeles, California 90089, Department of Chemistry, University of Warwick, Coventry CV4 7AL, West Midlands, UK, and Department of Chemistry, Iowa State University, Ames, Iowa

## Abstract

*Ab initio* molecular orbital theory has been used to calculate accurate enthalpies of formation and adiabatic electron affinities or ionization potentials for  $N_3$ ,  $N_3^-$ ,  $N_5^+$ , and  $N_5^-$  from total atomization energies. Born-Haber cycle calculations, using estimated lattice energies and the adiabatic ionization potentials of the anions and electron affinities of the cations, permit for the first time reliable stability predictions for the hypothetical  $N_5^+N_3^-$  and  $N_5^+N_5^-$  salts. Contrary to previous predictions, it is shown that neither salt can be stabilized, decomposing spontaneously to  $N_3$  radicals and  $N_2$ . This conclusion was experimentally confirmed by low-temperature metathetical reactions between  $N_5SbF_6$  and alkali metal azides in different solvents, resulting in violent reactions with spontaneous nitrogen evolution. It is also shown that the vertical ionization potentials and electron affinities, used in previous stability predictions, must not be used in stability predictions involving species, such as  $N_5$  ions, because the resulting  $N_5$  radicals are not vibrationally stable and undergo spontaneous further decomposition. The use of the vertical values, that neglects this highly exothermic secondary decomposition of  $N_5$  to  $N_3$  and  $N_2$ , results in large errors of about 100 kcal/mol for each  $N_5$  unit. It is also shown that a previous

comparison of the density and energy density of hydrazine with those estimated for  $N_5^+N_5^-$  is significantly in error.

Authors to whom correspondence should be addressed. Electronic mail: david.dixon@pnl.gov;  
kchrste@usc.edu.

<sup>†</sup> PNNL

<sup>‡</sup> AFRL

<sup>#</sup> USC

<sup>§</sup> University of Warwick

<sup>††</sup> Iowa State

## Introduction

The discovery of stable  $N_5^+$  salts,<sup>1,2</sup> the long-known existence of stable  $N_3^-$  salts,<sup>3</sup> and the recent experimental detection of the  $N_5^-$  anion<sup>4</sup> have stimulated research in polynitrogen chemistry and a search for nitrogen allotropes. The high endothermicity of polynitrogen compounds renders their preparation and handling very difficult, and reliable stability predictions are important for the selection of suitable target compounds. Unfortunately, only the enthalpy of formation of  $N_2$  is well established. The enthalpies of formation of other crucial species, such as  $N_3$ ,  $N_3^-$ ,  $N_5$ ,  $N_5^+$  and  $N_5^-$ , are not accurately known. There have been a number of theoretical studies on allotropes of nitrogen using *ab initio* molecular orbital theory without the use of empirical parameters, but these studies have not reliably established the energetics of these compounds. In particular we note the important work of the Bartlett group on these species,<sup>5,6</sup> the work of Nguyen and Ha on decomposition mechanisms for  $N_5^x$ ,  $x = -1, 0, +1$ ,<sup>7</sup> and that of Martin and co-workers on  $N_3$ .<sup>8</sup>

We have developed an approach<sup>9</sup> to the reliable calculation of molecular thermodynamic properties, notably enthalpies of formation, based on *ab initio* molecular orbital theory without reliance on embedded empirical parameters. Our approach involves an accurate calculation of the total atomization energy of a molecule and combines this value with known enthalpies of formation of the atoms to calculate the molecular enthalpy of formation at 0 K. This method starts with coupled cluster theory, including a perturbative triples correction (CCSD(T)),<sup>10,11,12</sup> combined with the correlation-consistent basis sets<sup>13,14</sup> extrapolated to the complete basis set (CBS) limit to treat the correlation energy of the valence electrons. This step is followed by a number of smaller corrections that are presumed to be additive, including core-valence interactions and relativistic effects, both scalar and spin-orbit. Finally, one must include the zero point energy obtained either from experiment, theory, or some combination. The standard enthalpies of formation of compounds at 298 K can then be calculated from the 0 K value and other calculated properties by using standard thermodynamic and statistical mechanics expressions.<sup>15</sup>

Another important problem involves the reliable prediction of whether the combination of a stable polynitrogen cation, such as  $N_5^+$ , with a stable polynitrogen anion, such as  $N_3^-$ , can lead to a stable ionic nitrogen allotrope, such as  $N_5^+N_3^-$ . Whereas such predictions can be made with the help of suitable Born-Haber cycles, they require the availability of reliable values for the

lattice energies of the salts, the first ionization potential of the anion and the electron affinity of the cation, and an excellent knowledge of the nature and stability of the most likely decomposition products. Although several theoretical studies on the stability of  $N_5^+N_3^-$  and  $N_5^+N_5^-$  have been published,<sup>5,6,16</sup> none of these have used appropriate Born-Haber cycles and input data. Therefore, the most important question has not been answered conclusively. Is the lattice energies of these salts sufficient to stabilize them as solids and prevent a spontaneous electron transfer from the anion to the cation causing spontaneous decomposition? A further important question deals with the problem as to whether calculated vertical electron affinities and ionization potentials can be used for these predictions. For example, the vertical electron affinity calculated<sup>6</sup> for  $N_5^+$  differs significantly from the experimentally determined electron affinity,<sup>2</sup> and there appears to be confusion with regard to which value should be used for the stability predictions. This paper provides conclusive answers to these questions and, for  $N_5^+N_3^-$ , provides experimental data in support of our theoretical predictions.

### Experimental Section

*Caution! Reactions of  $N_5^+$  salts with azide ions are violent and can result in explosions. Therefore, these materials should be handled only on a small scale with appropriate safety precautions (face shield, leather gloves, and protective clothing).*

**Materials and Apparatus.** All reactions were carried out in a Teflon-PFA double U-tube apparatus that consisted of a reaction U-tube, a porous Teflon filter assembly, and a receiver U-tube. Volatile materials were handled on a stainless steel/Teflon-FEP vacuum line.<sup>17</sup> Nonvolatile solids were handled in the dry nitrogen atmosphere of a glove box. Infrared spectra were recorded on a Mattson Galaxy FT-IR spectrometer using dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded on a Bruker Equinox 55 FT-RA spectrometer using a Nd-YAG laser at 1064 nm and Pyrex melting point capillaries as sample containers.

The  $N_5SbF_6$  was prepared based on our previously reported procedure.<sup>2</sup> The  $CsN_3$  (Aldrich Chemical Company) was pretreated with an excess of  $(CH_3)_3SiN_3$  to remove any traces of moisture. The  $SO_2$  (Air Products) was used as received.

**Reactions of  $N_5SbF_6$  with  $CsN_3$ .** In a typical experiment,  $N_5SbF_6$  (2.285 mmol) and  $CsN_3$  (2.267 mmol) were loaded in the dry box into a Teflon-PFA reaction vessel that was closed by a Teflon valve. On the vacuum line, anhydrous  $SO_2$  (5.0 ml, liquid) was added at  $-196^\circ C$ . The reaction

mixture was warmed to the melting point of  $\text{SO}_2$  ( $-64^\circ\text{C}$ ). After the  $\text{SO}_2$  had partially melted and the slurry of reactants was gently agitated, a violent reaction took place producing a bright yellow flame. The reactor was quickly quenched with liquid nitrogen. A check for noncondensable gases at  $-196^\circ\text{C}$  revealed 9.05 mmol of  $\text{N}_2$  as expected for the complete decomposition of 2.267 mmol  $\text{N}_5\text{N}_3$  to  $\text{N}_2$ . Pumping off all volatiles at  $-64^\circ\text{C}$  produced 0.8890 g of a white solid residue (weight expected for 2.267 mmol  $\text{CsSbF}_6 = 0.836$  g). The extra weight was due to some residual  $\text{SO}_2$ . Raman and infrared spectra of the white solid, after pumping at room temperature, showed it to be pure  $\text{CsSbF}_6$ .

This reaction can be moderated by the separate dissolution of the starting materials in  $\text{SO}_2$  and the combination of the resulting clear solutions at  $-64^\circ\text{C}$ . Under these conditions, the decomposition reaction proceeded rapidly but without violence and gave the same results as described above.

**Reactions of  $\text{N}_5\text{SbF}_6$  with  $\text{CsN}_3$ .** To equimolar amounts of  $\text{NaN}_3$  and  $\text{N}_5\text{SbF}_6$ ,  $\text{CHF}_3$  was added as a solvent at  $-196^\circ\text{C}$ , and the resulting mixture was warmed to  $-95^\circ\text{C}$  and then to  $-64^\circ\text{C}$ . No  $\text{N}_2$  evolution was observed under these conditions. The  $\text{CHF}_3$  was pumped off at  $-95^\circ\text{C}$  and  $\text{SO}_2$  was added as a solvent at  $-196^\circ\text{C}$ . The mixture was warmed to  $-64^\circ\text{C}$ , but again no  $\text{N}_2$  evolution was observed. Pumping off the  $\text{SO}_2$  at  $-64^\circ\text{C}$  resulted in a white solid residue that, based on its room temperature Raman spectrum, consisted of a mixture of unreacted  $\text{NaN}_3$  and  $\text{N}_5\text{SbF}_6$ , indicating that no reactions had occurred due to the very low solubility of  $\text{NaN}_3$  in these solvents.

### Computational Approaches

**Enthalpies of Formation.** The augmented correlation consistent basis set aug-cc-pVnZ ( $n = \text{D, T, Q}$ )<sup>18</sup> was used for nitrogen. Only the spherical components (5-*d*, 7-*f*, 9-*g* and 11-*h*) of the Cartesian basis functions were used. This family of basis sets contains an additional shell (e.g. spd for DZ) of diffuse functions that are necessary for an accurate description of anions. Calculations were performed using the MOLPRO,<sup>19</sup> Gaussian,<sup>20</sup> and GAMESS<sup>21</sup> suites of programs. The open-shell CCSD(T) calculations were carried out at the R/UCCSD(T) level. In this approach, a restricted open shell Hartree-Fock (ROHF) calculation was initially performed in order to generate the set of molecular orbitals and the spin constraint was relaxed in the coupled cluster calculation.<sup>22,23,24</sup> The CCSD(T) total energies were extrapolated to the CBS limit by using a mixed exponential/Gaussian function of the form:

$$E(n) = E_{\text{CBS}} + A \exp[-(n-1)] + B \exp[-(n-1)^2] \quad (1)$$

with  $n = 2$  (aug-cc-pVDZ), 3 (aug-cc-pVTZ), etc., as first proposed by Peterson et al.<sup>25</sup> This extrapolation method has been shown to yield atomization energies in the closest agreement with experiment by a small measure as compared to other extrapolation approaches up through  $n = 4$ .<sup>8</sup>

Most geometries were optimized at the frozen core CCSD(T) level with various augmented correlation-consistent basis sets. With the exception of the  $\text{N}_5$  radical, all geometries were optimized with the aug-cc-pVTZ or aug-cc-pVQZ basis sets. If the CCSD(T)/aug-cc-pVQZ geometry was not available, the CCSD(T)/aug-cc-pVTZ geometry was used for the CCSD(T)/aug-cc-pVQZ calculation. Geometries for the  $\text{N}_5$  radicals were obtained from ZAPT2/6-311+G(2df) and CCSD(T)/aug-cc-pVDZ calculations. Vibrational frequencies were calculated at the CCSD(T) and MP2 levels with the aug-cc-pVDZ basis set. Calculations were performed on SGI, IBM and Apple G4 computers.

Core-valence corrections,  $\Delta E_{\text{CV}}$ , were obtained at the CCSD(T)/cc-pCVTZ level of theory.<sup>26</sup> Scalar relativistic corrections ( $\Delta E_{\text{SR}}$ ), which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms, were included at the CI-SD (configuration interaction singles and doubles) level of theory using the cc-pVTZ basis set.  $\Delta E_{\text{SR}}$  is taken as the sum of the mass-velocity and 1-electron Darwin (MVD) terms in the Breit-Pauli Hamiltonian.<sup>27</sup> Because N has a  $^4\text{S}$  ground state, there are no atomic spin orbit corrections to the total atomization energies. The spin orbit coupling constant for  $\text{N}_3$  is  $71.3 \text{ cm}^{-1}$  based on experiment<sup>28</sup> leading to a spin orbit correction of  $0.10 \text{ kcal/mol}$ .

By combining our computed  $\sum D_0$  values with the known enthalpies of formation<sup>29</sup> at 0 K for N of  $\Delta H_f^0(\text{N}) = 112.53 \pm 0.02 \text{ kcal mol}^{-1}$ , we can derive  $\Delta H_f^0$  values for the molecules under study in the gas phase. We obtain enthalpies of formation at 298 K by following the procedures outlined by Curtiss and coworkers<sup>15</sup> and by using the stationary electron convention, *i.e.*, we do not assume a change in the enthalpy of formation of the electron as a function of temperature.

**Lattice Energies.** For this study, we employ the equation<sup>30</sup>:

$$U_L = 2 I [\alpha V_m^{-1/3} + \beta] \quad (2)$$

to estimate the lattice energy,  $U_L$ , of the salts  $\text{N}_5^+\text{N}_5^-$  and  $\text{N}_5^+\text{N}_3^-$  from estimated ion volumes.  $I$  is the ionic strength ( $= 1$ ),  $V_m$  is the molecular (formula unit) volume of the lattices involved which is equal to the sum of the individual ion volumes of the cation,  $V_+$  and anion,  $V_-$  and  $\alpha$  and  $\beta$  take



the values  $28.0 \text{ kcal mol}^{-1} \text{ nm}$  and  $12.4 \text{ kcal mol}^{-1}$  respectively for 1:1 salts. The individual ion volumes can be estimated from an ion volume database,<sup>30</sup> inferred in some cases from established crystal structure data, or calculated. In order to calculate the volumes of the ions, we chose to use the volumes that we have used in free energy of solvation calculations.<sup>31</sup> The electron densities were calculated at the B3LYP/6-31+G\* level<sup>32</sup> and the volume was taken to be that inside the 0.001 a.u. contour of the electron density.

## Results and Discussion

### Calculated Geometries

The calculated geometries for the molecules,  $\text{N}_2$ ,  $\text{N}_3$ ,  $\text{N}_3^-$ ,  $\text{N}_5^-$ , and  $\text{N}_5^+$  are summarized in Table 1.

$\text{N}_2$ : As expected, the geometry for  $\text{N}_2$  at the CCSD(T)/aug-cc-pVQZ level is in excellent agreement with the experimental value.<sup>33</sup> Theory overestimates experiment by 0.0028 Å. For comparison purposes, we also optimized the N-N bond length with the larger aug-cc-pV5Z basis set. This produced a small 0.0010 Å decrease in the bond length, indicating that aug-cc-pVQZ bond lengths should be within approximately 0.001 Å of the basis set limit for the other molecules that could be treated at this level of theory. If the frozen core approximation is removed via calculations with the core/valence (CV) cc-pCVQZ basis set, another 0.0020 Å shortening of the bond length is observed. The final CCSD(T)/aug-cc-pV5Z + CV bond length of 1.0975 Å is almost identical to the experimental value at 1.0977 Å.

$\text{N}_3$ : The geometry for  $\text{N}_3$  ( $D_{\infty h}$ ) is in excellent agreement with the experimental value.<sup>34</sup> The calculations predict a value for the NN bond that is slightly shorter than the experimental value in contrast to  $\text{N}_2$  where the calculations predict a longer bond at the CCSD(T)/aug-cc-pVQZ level.

$\text{N}_3^-$ : The calculated geometry for  $\text{N}_3^-$  is also in very good agreement with experiment, with the calculated NN bond length again being slightly shorter than experiment.<sup>35</sup>

$\text{N}_5^+$ : The geometry for  $\text{N}_5^+$  has been measured in the crystal by x-ray diffraction techniques.<sup>2</sup> The calculated values are in good agreement with the crystal structure values considering the uncertainty in the experimental values and the different environment. The calculated geometrical parameters for  $\text{N}_5^+$  are the same as those reported by Fau and Bartlett at the CCSD(T)/aug-cc-pVTZ level,<sup>5</sup> whereas the geometries calculated for  $\text{N}_3^-$  at the same level differ slightly.

$N_5^-$ : The value of 1.334 Å calculated for the NN bond length in  $N_5^-$  at the CCSD(T)/6-311+(G(d,p) level<sup>7</sup> lies between our values calculated at the CCSD(T) level with the aug-cc-pVDZ and aug-cc-pVTZ basis sets, respectively.

$N_5$  (open isomer): ZAPT2<sup>36</sup> calculations with the 6-311+G(2df) basis set followed by CCSD(T)/cc-pVTZ single point calculations confirm previous conclusions<sup>7</sup> that the  $N_5$  radical starting from this geometry is vibrationally unstable. Starting from the optimized  $N_5^+$  structure, the neutral species dissociates without a barrier to  $N_3 + N_2$  as shown in Figure 1.

$N_5$  (cyclic isomer): The  $N_5$  radical cyclic isomer would be generated by detaching an electron from cyclic  $N_5^-$ . The HOMO of  $N_5^-$  is a degenerate in-plane orbital involving essentially lone pair interactions. Production of the  $N_5$  radical leads to  $(e)^3$  occupancy which Jahn-Teller distorts to a  $C_{2v}$  structure. Two states can be derived from the  $(e)^3$  occupancy, a  $^2A_1$  state and a  $^2B_1$  state (a  $^2B_2$  state would be a  $\pi$  radical). The geometry for the cyclic  $N_5$  ( $C_{2v}$ )  $^2A_1$  radical was found to be a stationary point on the ZAPT2/6-311+G(2df) potential energy surface. The cyclic  $N_5$  radical at the ZAPT2/6-311+G(2df) geometry is 66.8 kcal/mol above the  $N_3 + N_2$  asymptote at the CCSD(T)/cc-pVTZ level. The longest NN ZAPT/6-311+G(2df) bond distance is that in the base of the pentagon, 1.354 Å. The shortest NN bonds are those connected to the apex, 1.292 Å. We took this geometry and initiated an optimization at the R/UCCSD(T)/aug-cc-pVDZ level for both the  $^2A_1$  and  $^2B_1$  states under the constraint of  $C_{2v}$  symmetry. The  $^2B_1$  state smoothly dissociated to the  $N_3 + N_2$  asymptote showing that on the CCSD(T)/aug-cc-pVDZ surface, this state is not a minimum. The  $N_3$  distance converges faster than the  $N_2$  distance. The  $^2A_1$  state is difficult to optimize but finally optimizes to a structure with 2 elongated  $N_2$  molecules complexed weakly to an N atom (see Table 1) as it cannot go to the products  $N_2 + N_3$ . At the CCSD(T)/aug-cc-pVTZ level at the optimized CCSD(T)/aug-cc-pVDZ geometry, the  $^2A_1$  state is 60.2 kcal/mol above the  $N_2 + N_3$  asymptote. These calculations strongly suggest that on electron detachment from  $N_5^-$ , the resulting radical has a path on the  $^2B_1$  surface that leads directly to the  $N_3 + N_2$  asymptote and that there is no stable cyclic  $N_5$  radical structure as already noted previously.<sup>7</sup> Frenking and co-workers as part of a study of  $Fe(\eta^5-N_5)_2$  report a structure for the  $^2A_1$  state of the  $N_5$  radical at the B3LYP/6-31G(d) level which could be a minimum although the structure is not discussed.<sup>37</sup>

### Calculated Frequencies

The calculated vibrational frequencies for  $N_2$ ,  $N_3$ ,  $N_3^-$ ,  $N_5^-$ ,  $N_5$  (cyclic) and  $N_5^+$  are summarized in Table 2.

**$N_2$ :** The harmonic frequency at the frozen core CCSD(T)/aug-cc-pVQZ level is within 5  $\text{cm}^{-1}$  of the experimental value.<sup>33</sup> Even at the CCSD(T)/aug-cc-pVTZ level, the  $N_2$  frequency is within 20  $\text{cm}^{-1}$  and is within 40  $\text{cm}^{-1}$  at the CCSD(T)/aug-cc-pVDZ level. This level of agreement is in part fortuitous. Whereas the aug-cc-pV5Z basis set frequency is identical to the experimental value, introduction of core/valence correlation increases  $\omega_e$  by 9.2  $\text{cm}^{-1}$ . Thus, the final CCSD(T)/aug-cc-pV5Z + CV value is 9  $\text{cm}^{-1}$  larger than experiment.

**$N_3$ :** For  $N_3$ , the frequencies calculated at the MP2/aug-cc-pVDZ level are in qualitative agreement with the experimental values<sup>38</sup> for the  $\pi$  bend and the symmetric stretch and in good agreement for the antisymmetric stretch. In this case, we have used the experimental frequencies to calculate the zero point energy.

**$N_3^-$ :** For  $N_3^-$ , the calculated antisymmetric harmonic stretch is in excellent agreement with the gas phase experimental value.<sup>34,39</sup> The value for the  $\nu_2$  bending frequency for this ion has been measured in the solid and a free space estimate for  $\nu_1$  has been obtained based on the spectrum measured in the solid.<sup>40,41</sup> For this ion, we used the experimental frequencies for the zero point energy determination. Use of the theoretical frequencies introduces a difference of 0.19 kcal/mol because the calculated bend and antisymmetric stretch are  $\sim 50 \text{ cm}^{-1}$  lower than the experimental values. The frequencies calculated by us for  $\nu_1$  and  $\nu_3$  are in reasonable agreement with those previously calculated at the CASPT2 level<sup>16</sup> and at the CEPA level.<sup>41</sup>

**$N_5^-$ :** For this ion, we used the frequencies calculated at the CCSD(T)/aug-cc-pVDZ level for the zero point energy calculation as there are no experimental values. Quite good agreement is found for the frequencies of  $N_5^-$  calculated at the MP2/aug-cc-pVDZ level and at the CCSD(T)/aug-cc-pVDZ level. The CASPT2 frequencies<sup>16</sup> are similar to our values.

**$N_5$  (cyclic isomer):** Frequencies were calculated at the ZAPT2/6-311+G(2df) level of theory for the  $^2A_1$  state. No experimental values are available for this species. As noted above, the  $^2B_1$  structure is not a minimum for the cyclic radical at the R/UCCSD(T)/aug-cc-pVDZ level.

**$N_5^+$ :** For  $N_5^+$ , there is reasonable agreement between the frequencies calculated at the MP2/aug-cc-pVDZ level and the average of the frequencies taken from measurements in the solid state.<sup>2</sup> The largest discrepancy is found for the highest frequency  $b_2$  mode with a difference of  $\sim 140 \text{ cm}^{-1}$ . The calculated  $a_2$  and  $b_1$  modes deviate by  $\sim 50 \text{ cm}^{-1}$  from the experimental values.

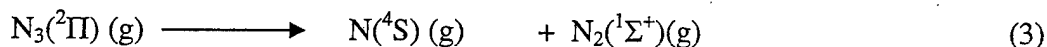
The fact that the differences cancel out leads to calculated and experimental zero point energies that are essentially identical. We used the average experimental values in our zero point energy calculations. Our calculated frequencies are in qualitative agreement with those calculated at the CCSD(T)/6-311+G(2d) and B3LYP/6-311+G(2d) levels.<sup>1,2</sup> The CCSD(T) values are in general lower than our MP2 values except for the  $a_2$  and  $b_1$  modes which are higher. The CASPT2 frequencies differ from ours more than might be expected, especially for the two highest modes.<sup>16</sup>

### Calculated Enthalpies of Formation

The total atomization energies are given in Table 3. The  $\Delta H_f^0$  values were converted to 298 K following the procedure of Curtiss and coworkers.<sup>15</sup>

**N<sub>2</sub>:** As shown in Table 3, the error in the atomization energy of N<sub>2</sub> is 0.76 kcal mol<sup>-1</sup> when compared to experiment.<sup>29</sup> This leads to an error in the calculated enthalpy of formation at 0 K of 0.76 kcal mol<sup>-1</sup>. We can thus estimate that the error bars in our heats of formation are likely to be on the order of  $\pm 1$  kcal/mol.

**N<sub>3</sub>:** The enthalpy of formation of N<sub>3</sub> has been reported by a number of authors. The NIST value<sup>29</sup> of  $100 \pm 5$  kcal mol<sup>-1</sup> at 0 K is almost 10 kcal mol<sup>-1</sup> below our calculated value. Our calculated value of 109.3 kcal mol<sup>-1</sup> is in much better agreement with the value of  $112 \pm 5$  based on the experimental measurement of the acidity of HN<sub>3</sub> and the measurement of the electron affinity of N<sub>3</sub>.<sup>42,43</sup> Our value of 109.3 kcal mol<sup>-1</sup> is in excellent agreement with the scaled value of 109.25 kcal mol<sup>-1</sup> given by Martin et al.<sup>8</sup> The calculated atomization energies show that reaction (3)



is only 4 kcal mol<sup>-1</sup> endothermic at 0 K.

**N<sub>3</sub><sup>-</sup>:** The enthalpy of formation of N<sub>3</sub><sup>-</sup> has been determined from gas phase acidity measurements and the enthalpy of formation of HN<sub>3</sub> to be  $48 \pm 2$  kcal mol<sup>-1</sup>.<sup>42</sup> This value is in excellent agreement with our calculated value of 47.2 kcal mol<sup>-1</sup>. Fau and Bartlett calculated the enthalpy of formation of N<sub>3</sub><sup>-</sup> by a variety of methods.<sup>5</sup> Their best estimated enthalpy of formation of 47.8 kcal mol<sup>-1</sup> is in good agreement with our value, although we note that their CCSD(T)/aug-cc-pVTZ value of 45.7 kcal mol<sup>-1</sup> is too low by 1.5 kcal mol<sup>-1</sup>. The electron affinity of N<sub>3</sub> has been measured to be  $2.68 \pm 0.01$  eV.<sup>43</sup> Our calculated adiabatic electron

affinity of 2.69 eV is in excellent agreement with this result. With an ANO (4s3p2d1f) basis set, the CASPT2 electron affinity was predicted to be 2.64 eV.<sup>16</sup>

$N_5^+$ : The enthalpy of formation of  $N_5^+$ , calculated by us, is 353.4 kcal mol<sup>-1</sup>. This result is in reasonable agreement with the value of 347.1 kcal mol<sup>-1</sup>, calculated by Fau and Bartlett at a lower level.<sup>5</sup> Christe and co-workers<sup>1,2</sup> predicted the enthalpy of formation of  $N_5^+$  to be 351.1 kcal mol<sup>-1</sup> at the CCSD(T) level with a polarized double zeta basis set. Nguyen and Ha predict a heat of formation of  $351.3 \pm 3.6$  kcal/mol based on CCSD(T)/6-311+ G(3df) calculations and the experimental energy of  $N_3$ .<sup>7</sup>

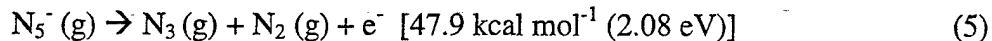
Our value for  $N_5^+$  can be used to estimate the adiabatic electron affinity of reaction (4).



The intermediate  $N_5$  radical starting from the  $N_5^+$  geometry (open structure) is unstable and will spontaneously dissociate to the first stable dissociation products,  $N_3(g) + N_2(g)$ , which will only form a weakly bound van der Waals complex with a binding energy on the order of less than 1 kcal mol<sup>-1</sup>. Thus, the energy of reaction (4) provides the adiabatic electron affinity of  $N_5^+$ . Our calculated value of 243.3 kcal mol<sup>-1</sup> (10.55 eV) is much higher than the vertical electron affinity of 6.04 eV reported by Fau et al<sup>5</sup> or the adiabatic ionization energy of  $7.4 \pm 0.2$  eV reported by Nguyen and Ha,<sup>7</sup> but in excellent agreement with our experimental bracketing study<sup>2</sup> that showed the electron affinity of  $N_5^+$  to fall between 10.52 and 11.48 eV. In the calculation of vertical electron affinities or ionization potentials, the geometries of the original species are retained for the products. Therefore, vertical electron affinities or ionization potentials should not be used for thermochemical calculations. Only when the direct reaction products are vibrationally stable species with geometries similar to those of the starting materials, will their vertical EA or IP values approximate the adiabatic values. If this is not the case, and the products can undergo further decomposition that does not involve any significant activation energy barrier, then the decomposition energy to the first well defined, vibrationally stable products must be added to the vertical electron affinity or ionization energy values.

$N_5^-$ : The enthalpy of formation of  $N_5^-$  is calculated to be 62.2 kcal mol<sup>-1</sup>, in excellent agreement with the value of  $62.1 \pm 3.6$  kcal/mol given by Nguyen and Ha.<sup>7</sup> This value can be used to calculate the adiabatic ionization potential of  $N_5^-$  in the same manner as discussed above for  $N_5^+$ . As noted above, loss of an electron from the degenerate HOMO of  $N_5^-$  leads to either a

$^2B_1$  or a  $^2A_1$  radical. We have shown that formation of the  $^2B_1$  radical provides a pathway leading to  $N_3 + N_2$  so the following channel (Reaction (5)) represents the adiabatic ionization process:



Use of this channel gives an adiabatic ionization potential of  $N_5^-$  of 2.08 eV. This is much lower than the vertical ionization potential of 5.58 eV reported by Fau et.al<sup>6</sup> or of 5.7 eV as given by Nguyen and Ha.<sup>7</sup> Nguyen and Ha do suggest that the cyclic  $N_5$  radical will spontaneously dissociate to  $N_3 + N_2$ . As shown below, the use of vertical instead of the appropriate adiabatic electron affinity and ionization potential values in the Born-Haber cycles dramatically influences the stability predictions for species containing either  $N_5^+$  or  $N_5^-$  ions. For a salt, such as  $N_5^+N_5^-$ , containing two  $N_5$  ions, the error could be doubled in the Born-Haber cycle calculations

The important dissociation channel for  $N_5^-$  is the formation of  $N_3^- + N_2$ . We predict this channel to be exothermic by 14.2 kcal mol<sup>-1</sup> at 0 K. This value is in good agreement with the value of 14.3 kcal mol<sup>-1</sup> reported by Nguyen and Ha at the CCSD(T)/aug-cc-pVTZ level.<sup>7</sup> It is important to know if there is a barrier separating  $N_5^-$  from the asymptotic products  $N_3^-$  and  $N_2$ . Nguyen and Ha calculated the energy barrier to dissociation as 27.7 kcal mol<sup>-1</sup> at the CCSD(T)/aug-cc-pVTZ level including zero point corrections based on a geometry calculated at the CCSD(T)/6-311+G(d) level.<sup>7</sup> We have calculated the energy of the transition state at the CCSD(T)/CBS level with Nguyen and Ha's geometry and with the geometry optimized by us at the MP2/aug-cc-pVDZ level. We calculated the geometry at the latter level in order to get a value of the zero point energy as well as the value of the imaginary frequency characterizing the transition state. The results are given in Tables 1 to 3. Our calculated energy barrier using the MP2 geometry is 29.4 kcal mol<sup>-1</sup> and when the zero point energy difference is included, the barrier is 27.2 kcal mol<sup>-1</sup>. The energy barrier using the Nguyen and Ha geometry is 0.61 kcal mol<sup>-1</sup> higher in energy than our value based on the MP2 geometry showing that the two geometries give essentially identical barrier heights. The barrier calculated<sup>7</sup> by Nguyen and Ha is very similar to our CCSD(T)/CBS value using their geometry. At the CASPT2/ANO(4s3p2d) level, the barrier is predicted to be 26 kcal mol<sup>-1</sup> and the dissociation energy to  $N_3^-$  and  $N_2$  is predicted to be exothermic by 9 kcal mol<sup>-1</sup>,<sup>16</sup> 4 kcal mol<sup>-1</sup> lower than our value. A calculation of the imaginary frequency for the transition state of the  $N_5^-$  decomposition shows a large value of 862i cm<sup>-1</sup>, suggesting that the ion might be able to tunnel through the barrier to reach the products. We can make a crude estimate of the tunneling effect by using the Wigner

expression.<sup>44</sup> This leads to an enhancement of the dissociation rate by 1.7 at 298 K. This suggests that tunneling at least needs to be considered for predicting the stability of  $N_5^-$ . For lower temperatures, a larger tunneling effect would be expected.

### Lattice Energy Calculations

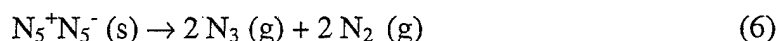
Prediction of lattice energies,  $U_L$  based on equation (2) requires an estimate of the relevant ion volumes and gave the following results:

$N_5^+N_3^-$ :  $V(N_5^+)$  is estimated to be  $0.051 (\pm 0.020) \text{ nm}^3$  based on the reported<sup>2</sup> crystal structure volume for  $N_5^+Sb_2F_{11}^-$  by subtraction of  $V(Sb_2F_{11}^-)$  (table 6, ref 30).  $V(N_3^-)$  is equal to  $0.058 (\pm 0.014) \text{ nm}^3$  (table 5, ref 30) and thus  $V(N_5^+N_3^-) = 0.109 (\pm 0.024) \text{ nm}^3$  leading to an estimate for  $U_L(N_5^+N_3^-) = 142 (\pm 7) \text{ kcal mol}^{-1}$ .

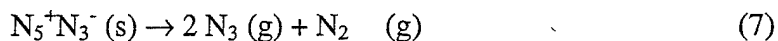
$N_5^+N_5^-$ : An upper limit for  $V(N_5^-)$  can be estimated from consideration of  $V(N_2)$  and  $V(N_3^-)$ . The volume of solid dinitrogen,  $V(N_2)$ , which is dimorphous,<sup>45</sup> can be obtained from crystal structure data for the  $\alpha$ -cubic and the hexagonal forms and averages to  $V(N_2) = 0.046 (\pm 0.001) \text{ nm}^3$ , leading to  $V(N_5^+N_5^-) = 0.155 (\pm 0.014) \text{ nm}^3$  giving a value for  $U_L(N_5^+N_5^-) = 129 (\pm 5) \text{ kcal mol}^{-1}$ . Alternatively, we can estimate the volume of the ions at the B3LYP/6-31+G\* level as described above:  $V(N_5^+) = 0.068 \text{ nm}^3$ ;  $V(N_5^-) = 0.088 \text{ nm}^3$ ;  $V(N_3^-) = 0.065 \text{ nm}^3$ . These estimated volumes yield  $U_L(N_5^+N_5^-) = 129 \text{ kcal mol}^{-1}$  and  $U_L(N_5^+N_3^-) = 135 \text{ kcal mol}^{-1}$ , well within the above error limits. The corresponding lattice *enthalpy*,  $\Delta H_L$ , appropriate for use in the cycles of Figures 1 and 2 are  $U_L(N_5^+N_5^-) + 2RT$  and  $U_L(N_5^+N_3^-) + 3/2RT$  respectively.

### Stability Predictions Using Born-Haber Cycles

For a chemical reaction to proceed spontaneously, its free energy change must be zero or negative. The decomposition of  $N_5^+N_5^-$  (s) is given by



and that for  $N_5^+N_3^-$  (s) by reaction (7)



The contribution from the  $T\Delta S$  term (entropy change) to the free energy for the reactions considered in this paper is always negative. We can estimate the entropy change for reactions (6) and (7) as follows. The entropy for the solid is not known but we can use the entropies of  $NH_4^+NO_3^-$  and  $NH_4^+N_3^-$ , which are 36 and 27 cal/mol K,<sup>46</sup> respectively, to estimate the value for the  $N_5^+$  salts. Given the well-established entropies of  $N_2$  and  $N_3$  of 45.8 and 54.1 cal/mol K respectively, we obtain at 298 K for reaction (6)  $-T\Delta S = -49 \text{ kcal/mol}$  if the entropy of

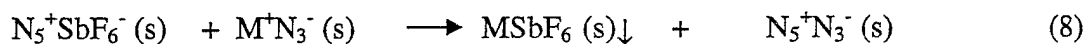
$\text{NH}_4^+\text{NO}_3^-$  is used to estimate that of the solid, and  $-\text{T}\Delta\text{S} = -51$  kcal/mol if the entropy of  $\text{NH}_4^+\text{N}_3^-$  is used. For reaction (7), the respective values are  $-\text{T}\Delta\text{S} = -35$  and  $-38$  kcal/mol at 298 K. Thus a significantly positive value for the reaction enthalpy would be required for  $\text{N}_5^+\text{N}_5^-$  and  $\text{N}_5^+\text{N}_3^-$  to be stable.

The enthalpy of a decomposition reaction of an ionic solid to gaseous decomposition products can be estimated from simple Born-Haber cycles (see Figures 2 and 3), provided the lattice energy ( $U_L$ ) of the solid, the adiabatic first ionization potential (IP) of the anion, and the adiabatic electron affinity (EA) of the cation are known. If the free energy change,  $\Delta G_r$ , of the decomposition reaction (6) is positive, *i.e.*, the decomposition products are higher in energy than the ionic solid, this value represents the minimum dissociation energy barrier, but one should keep in mind that the actual barrier can well be higher than  $\Delta G_r$ . If, however, the free energy change is negative, spontaneous decomposition occurs. The potential energy curves for both scenarios are depicted in Figure 4 for  $\text{N}_5^+\text{N}_5^-$ . The left curve represents the case of the enthalpy of reaction (6) being negative, resulting in spontaneous decomposition of the solid to the first vibrationally stable intermediates, that is,  $\text{N}_3$  radicals and  $\text{N}_2$ . The energy values used for the left curve are the actual numbers calculated in the present study and demonstrate that there is no barrier stabilizing  $\text{N}_5^+\text{N}_5^-$  against spontaneous decomposition.

The right curve of Figure 4 represents the scenario of a positive reaction enthalpy and the only condition under which solid  $\text{N}_5^+\text{N}_5^-$  might be isolated. This is a hypothetical case, assuming the enthalpy of formation of  $\text{N}_5^+\text{N}_5^-$  being about  $100 \text{ kcal mol}^{-1}$  more negative than the calculated value. If the values for the IP of  $\text{N}_5^-$  and the EA of  $\text{N}_5^+$  are fixed, the lattice energy of  $\text{N}_5^+\text{N}_5^-$  would have to be about  $100 \text{ kcal/mol}$  higher than our calculated value which is impossible based on the molar volumes of the ions involved. The relatively small uncertainties in our  $\Delta H_f$  values,  $-65 \pm 7 \text{ kcal mol}^{-1}$  for  $\text{N}_5^+\text{N}_5^-$  and  $-39 \pm 9 \text{ kcal mol}^{-1}$  for  $\text{N}_5^+\text{N}_3^-$ , together with the large  $-\text{T}\Delta\text{S}$  terms, allow us to predict with confidence that both compounds cannot be stabilized in the form of ionic solids.

### Experimental Results and their Comparison with the Predictions

All of our attempts to prepare solid  $\text{N}_5^+\text{N}_3^-$  by the metathesis reaction (8) failed.





In liquid  $\text{SO}_2$ , the  $\text{N}_5^+\text{SbF}_6^-$  salt is highly soluble. Using very soluble (solubility at  $-64^\circ\text{C} = 3.14 \times 10^{-3} \text{ mol mL}^{-1}$ )  $\text{CsN}_3$ , violent reactions occurred resulting in quantitative formation of poorly soluble (solubility at  $-64^\circ\text{C} = 6.56 \times 10^{-6} \text{ mol mL}^{-1}$ )  $\text{CsSbF}_6$  and  $4 \text{ N}_2$ . Using poorly soluble (solubility at  $-64^\circ\text{C} = 9.23 \times 10^{-5} \text{ mol mL}^{-1}$ )  $\text{NaN}_3$ , the metathesis did not proceed to any measurable extent, and unreacted  $\text{NaN}_3$  and  $\text{N}_5\text{SbF}_6$  were recovered. It was also shown that solid  $\text{NaN}_3$  and  $\text{N}_5\text{SbF}_6$  can be mixed as dry powders at room temperature and the Raman spectrum of the mixture can be recorded without evidence of reaction provided that the laser power is kept at a low level. Attempts to carry out the metathesis in  $\text{CHF}_3$  solution were also unsuccessful because of the low solubility of the starting materials in this solvent. These experiments show that in all cases where metathesis took place, only spontaneous decomposition was observed and, thus, confirm the above given theoretical predictions.

#### Assessment of the Performance of Solid $\text{N}_5^+\text{N}_5^-$ as a Monopropellant

In a previous publication on the stability of  $\text{N}_5^+\text{N}_5^-$ ,<sup>6</sup> it was claimed that this compound, if it "could be stabilized, would be an ideal monopropellant since its density is nearly twice that of hydrazine while the energy densities (heat of reaction per gram) are comparable." This claim has received worldwide attention as a potential revolution in rocket propulsion.<sup>47</sup> Even if one ignores the incorrect use of the vertical instead of the adiabatic electron affinities and ionization potentials in the previous work, which as shown above could lead to incorrect stability predictions, the statements concerning the densities and energy densities are incorrect. Whereas the previous energy density estimate<sup>6</sup> of  $2.11 \text{ kcal/g}$  for  $\text{N}_5^+\text{N}_5^-$  is in fair agreement with our estimate of  $1.98 \text{ kcal/g}$ , the maximum energy density value for hydrazine is not comparable to this value at all. Even if one assumes its decomposition to proceed as shown in equation (9),



the maximum energy density of  $\text{N}_2\text{H}_4$  would be only  $1.17 \text{ kcal/g}$ .<sup>29</sup> The actual value, however, is significantly lower because there is always some decomposition of  $\text{NH}_3$  to  $\text{N}_2$  and  $\text{H}_2$ .<sup>45</sup> Hence, the energy densities of  $\text{N}_5^+\text{N}_5^-$  and  $\text{N}_2\text{H}_4$  are not comparable but differ by a factor of 2. The density of  $\text{N}_2\text{H}_4$  is very close to  $1.0 \text{ g/cm}^3$ .<sup>48</sup> The previous prediction that  $\text{N}_5^+\text{N}_5^-$  should have twice this density does not agree with our predictions. Based on our molar volume estimates, the density of  $\text{N}_5^+\text{N}_5^-$  should be only  $1.50 \text{ g/cm}^3$ . While the conclusion<sup>6</sup> that a hypothetical polynitrogen compound, such as  $\text{N}_5^+\text{N}_5^-$ , would be an excellent monopropellant for rocket

propulsion or explosive is certainly correct and has been known for many years, the values given in reference 6 are badly flawed.

## Conclusions

Our results are remarkable in many respects, including the following points.

- (i): Our results provide the first conclusive quantitative predictions concerning the stability of  $N_5^+N_5^-$  and  $N_5^+N_3^-$ . They show that both compounds cannot be stabilized in the solid state. In spite of detailed calculations, the previous papers<sup>5,6,16</sup> dealing with these problems did not use rigorous approaches involving appropriate Born-Haber cycles, which prevented any firm conclusions from being made.
- (ii): Our results also show that for species, such as  $N_5^+$  and  $N_5^-$ , it is imperative to use adiabatic ionization potentials and electron affinities. Vertical electron affinities and ionization potentials, obtained by *ab initio* calculations, must not be employed for these predictions and lead to erroneous conclusions. For example, use of our lattice energy values for  $N_5^+N_5^-$  and  $N_5^+N_3^-$ , if combined with the published<sup>5</sup> vertical ionization potential of  $N_5^-$  (5.58 eV) and  $N_3^-$  (2.53 eV) and the vertical electron affinity of  $N_5^+$  (6.04 eV) would result in the salts  $N_5^+N_5^-$  and  $N_5^+N_3^-$  having large positive  $\Delta H_f$  values with minimum decomposition enthalpy barriers of 123 kcal mol<sup>-1</sup> and 65 kcal mol<sup>-1</sup>, respectively. They therefore would lead to the incorrect conclusion<sup>5</sup> that these salts exhibit extraordinary stability.
- (iii): In view of the instability of the  $N_5$  radical and its strongly exothermic spontaneous decomposition to  $N_3$  radicals and  $N_2$ , both,  $N_5^+$  and  $N_5^-$ , are less than ideal choices for preparing a stable ionic nitrogen allotrope.
- (iv): Contrary to previous predictions,<sup>5</sup>  $N_5^+N_5^-$  is less stable than  $N_5^+N_3^-$ , because the former contains two  $N_5$  species.
- (v): Stability calculations for individual ions or ion pairs do not provide sufficient information for stability predictions. Rigorous Born-Haber cycles, including realistic lattice energy estimates, and an evaluation of the stability of the decomposition products are required to make meaningful predictions.
- (vi): Our theoretical predictions concerning the instability of  $N_5^+N_3^-$  and the use of the adiabatic electron affinities and ionization potentials were confirmed by extensive experimental studies involving the low-temperature metathesis of  $N_5^+SbF_6^-$  with

different alkali metal azides in various solvents. In all cases where metathesis took place, only spontaneous decomposition to  $N_2$  was observed.

- (vii): The previous conclusions<sup>6</sup> concerning the energy densities and densities of hydrazine and  $N_5^+N_5^-$  are not correct.

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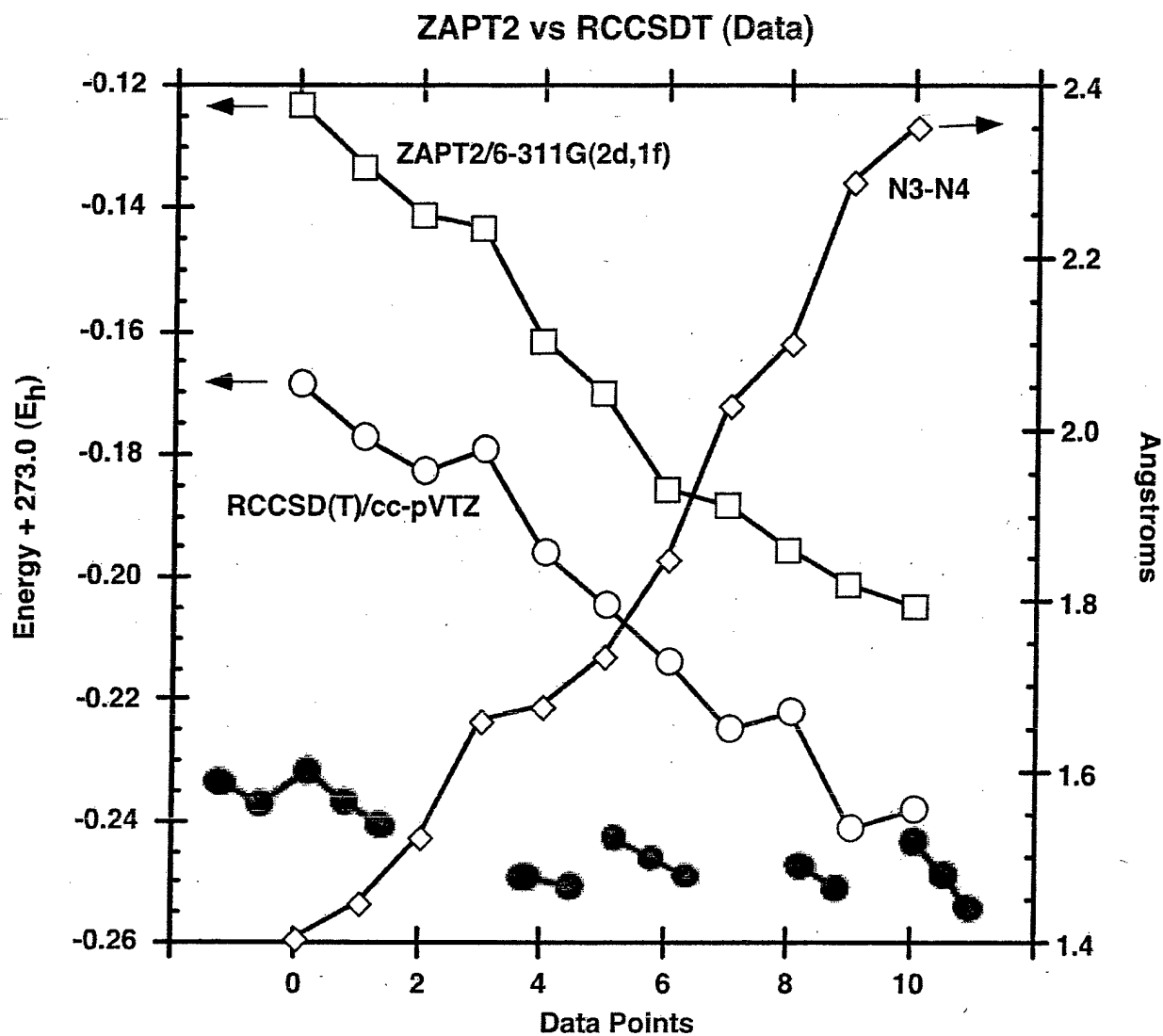
### Figure Captions

Figure 1. Schematic showing the decomposition of the  $N_5$  radical formed by electron attachment to  $N_5^+$  at the ZAPT2/6-311G(2d,f) and CCSD(T)/cc-pVTZ levels. The radical smoothly dissociates to products. The x axis corresponds to the calculation number describing the dissociation and the y axis corresponds to the energy or to the N3 – N4 (numbered starting from the right) interaction distance representing the separation between the  $N_2$  and  $N_3$  molecules. The large squares correspond to the ZAPT/6-311G(2d,1f) potential energy surface and the circles correspond to the CCSD(T)/cc-pVTZ potential energy surface. The small squares represent the N3-N4 distance which increases.

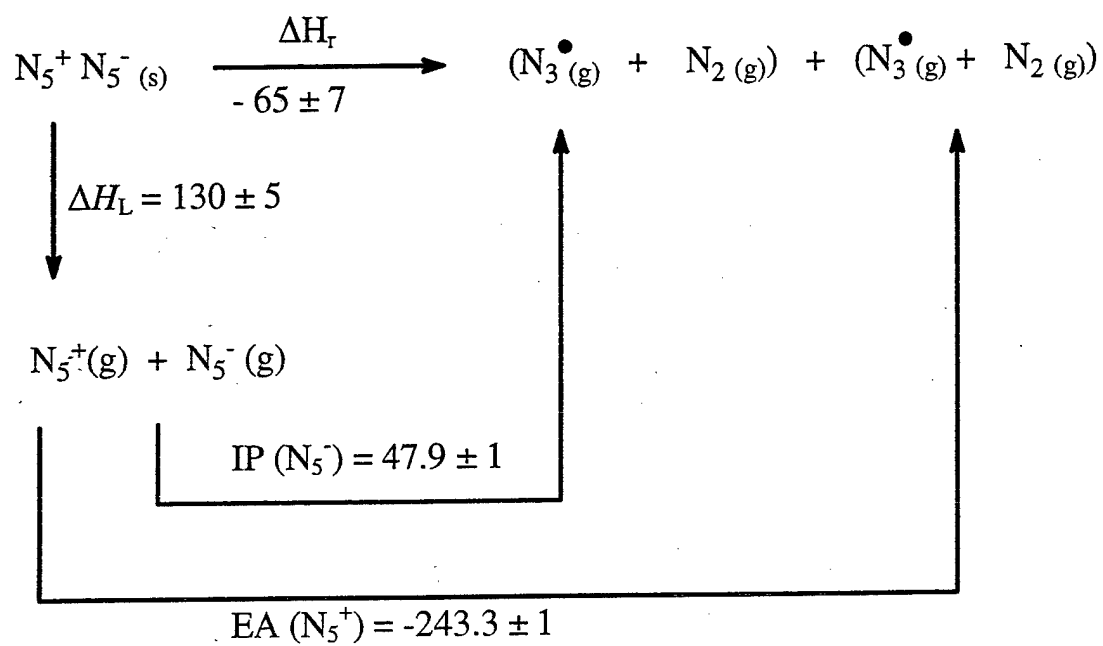
Figure 2. Born-Haber cycle in  $\text{kcal mol}^{-1}$  for the decomposition reaction of solid  $N_5^+N_5^-$ . The large negative value for  $\Delta H_f$  demonstrates the unlikelihood of this salt to exist.

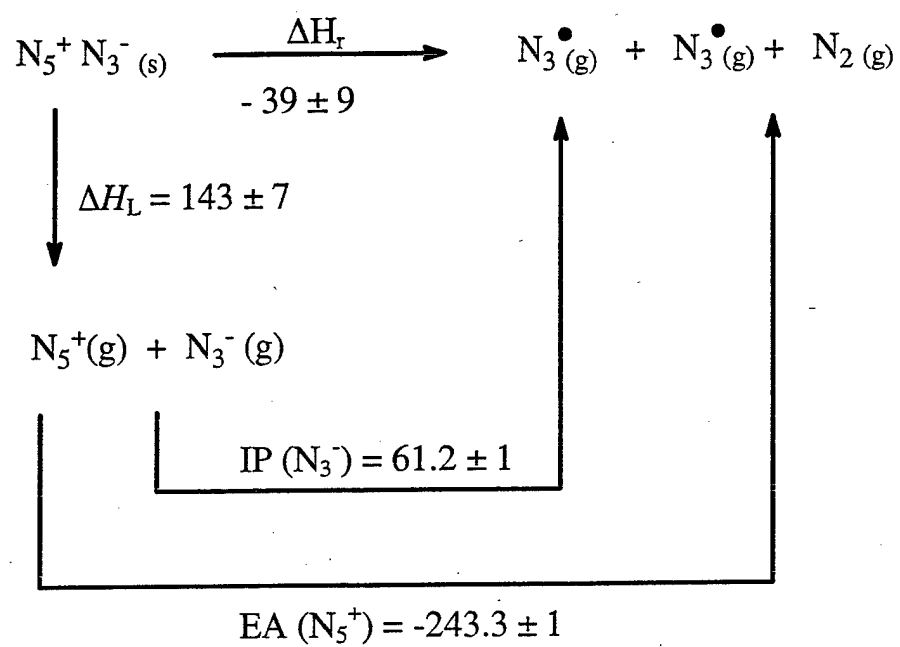
Figure 3. Born-Haber cycle in  $\text{kcal mol}^{-1}$  for the decomposition reaction of solid  $N_5^+N_3^-$ . The large negative value for  $\Delta H_f$  demonstrates this salt is also unlikely to exist.

Figure 4. Potential energy curves in  $\text{kcal mol}^{-1}$  for the decomposition reaction of solid  $N_5^+N_5^-$  to dinitrogen. The left curve is based on the calculated values from this study and shows that a hypothetical  $N_5^+N_5^-$  would spontaneously decompose to  $2 N_3 (g) + 2 N_2 (g)$ . The right curve shows that for  $N_5^+N_5^-$  to be stable, its enthalpy of formation would have to be significantly lower than those of the gaseous species ( $2 N_3 + 2 N_2$ ).





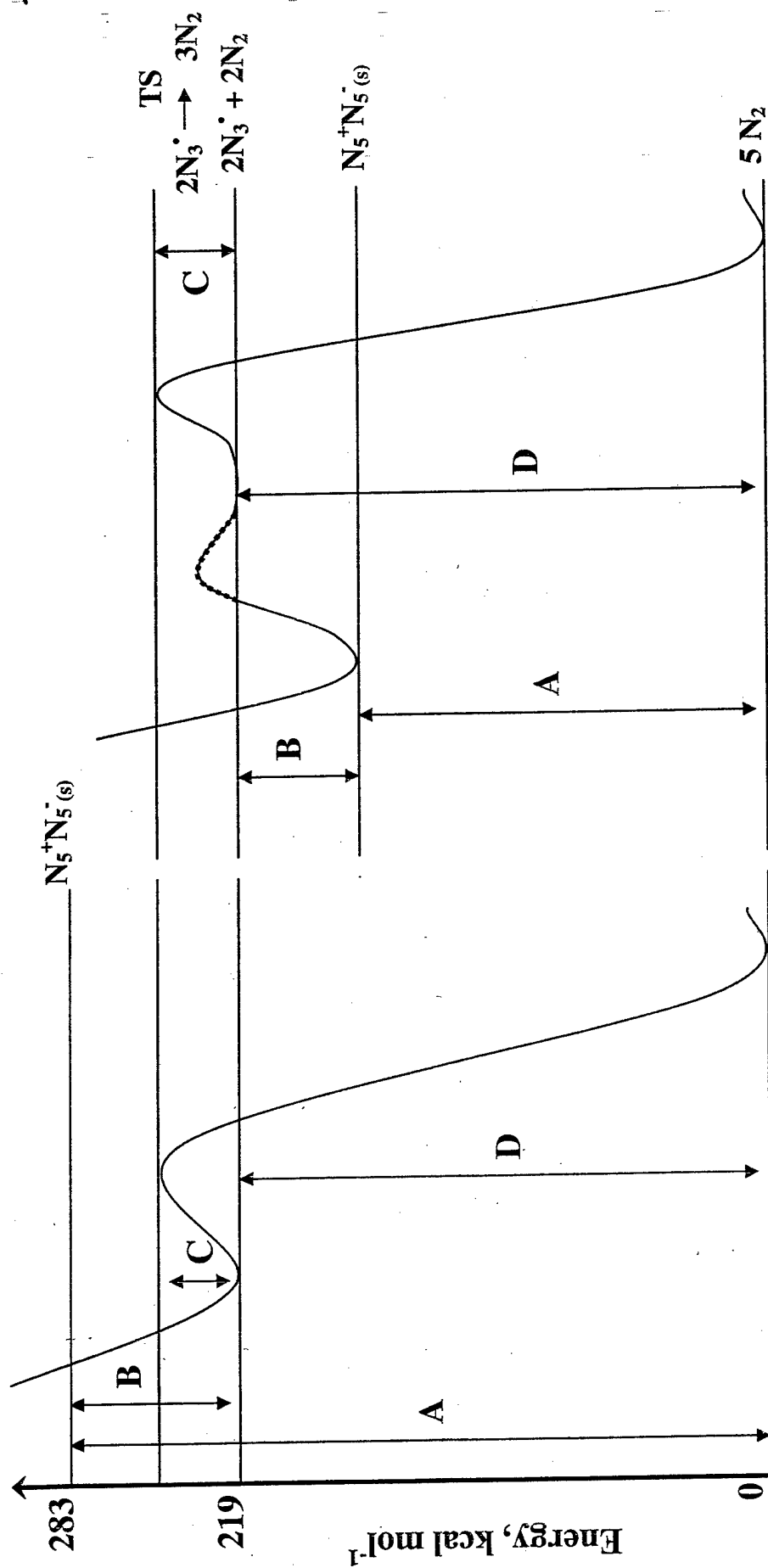






NEGATIVE B VALUE, KINETICALLY  
UNSTABLE, REPRESENTS CALCD VALUES

POSITIVE B VALUE AND KINETIC STABILITY  
WOULD REQUIRE  $\Delta H_f(N_5^+N_5^-(s)) \approx 180 \text{ kcal/mol}$



$$A = \Delta H_f(N_5^+N_5^-(s))$$

$$B = \Delta H_r(N_5^+N_5^-(s) \longrightarrow 2N_3^\cdot + 2N_2(g)) = U_L(N_5^+N_5^-(s)) + 2RT + IP(N_5^-(g)) - EA(N_5^+(g))$$

$$C = \text{Activation energy barrier for decomposition of } 2N_3^\cdot \longrightarrow 3N_2(g)$$

$$D = \Delta H_r(2N_3^\cdot \longrightarrow 3N_2(g))$$



**Table 1.** Calculated Valence Correlated Geometries  $N_m^x$ .<sup>a</sup>

| Species                        | Basis                           | r(NN)               | $\theta$ (NNN)     |
|--------------------------------|---------------------------------|---------------------|--------------------|
| $N_2(\tilde{X}^1A)$            | CCSD(T)/aug-cc-pVDZ             | 1.1209              |                    |
|                                | CCSD(T)/aug-cc-pVTZ             | 1.1040              |                    |
|                                | CCSD(T)/aug-cc-pVQZ             | 1.1005              |                    |
|                                | CCSD(T)/aug-cc-pV5Z             | 1.0995 <sup>b</sup> |                    |
|                                | Expt <sup>33</sup>              | 1.0977              |                    |
| $N_3(\tilde{X}^2\Pi_g)$        | CCSD(T)/aug-cc-pVDZ             | 1.1997              | 180.0 <sup>c</sup> |
|                                | CCSD(T)/aug-cc-pVTZ             | 1.1840              |                    |
|                                | CCSD(T)/aug-cc-pVQZ             | 1.1802              |                    |
|                                | Expt <sup>34</sup>              | 1.18115             |                    |
| $N_3^-(\tilde{X}^1\Sigma_g^+)$ | CCSD(T)/aug-cc-pVDZ             | 1.2072              | 180.0 <sup>c</sup> |
|                                | CCSD(T)/aug-cc-pVTZ             | 1.1912              |                    |
|                                | CCSD(T)/aug-cc-pVQZ             | 1.1876              |                    |
|                                | Expt <sup>35</sup>              | 1.1884              |                    |
| $N_5^-(\tilde{X}^1A_1)$        | CCSD(T)/aug-cc-pVDZ             | 1.3429              | 108.0 <sup>c</sup> |
|                                | CCSD(T)/aug-cc-pVTZ             | 1.3309              |                    |
| $N_5^+(\tilde{X}^1A_1)$        | CCSD(T)/aug-cc-pVDZ             | 1.1319              | 165.87             |
|                                |                                 | 1.3413              | 107.90             |
|                                | CCSD(T)/aug-cc-pVTZ             | 1.1159              | 167.08             |
|                                |                                 | 1.3238              | 108.48             |
|                                | Expt <sup>2</sup>               | 1.10                | 168.1              |
|                                |                                 | 1.30                | 111.2              |
| $N_5(^2A_1)^d$                 | ZAPT2/6-311+G(2df)              | 1.292               | 121.0              |
|                                |                                 | 1.343               | 100.1              |
|                                |                                 | 1.355               | 109.5              |
|                                | CCSD(T)/aug-cc-pVDZ             | 1.422               | 102.3              |
|                                |                                 | 1.165               | 137.7              |
|                                |                                 | 2.576               | 81.1               |
| $N_5^-$ -TS <sup>e</sup>       | MP2/aug-cc-pVDZ                 | 1.270               | 125.5              |
|                                |                                 | 1.702               | 99.4               |
|                                |                                 | 1.215               | 107.8              |
|                                | CCSD(T)/6-311+G(d) <sup>7</sup> | 1.252               | 128.9              |
|                                |                                 | 1.191               |                    |
|                                |                                 | 1.764               |                    |

<sup>a</sup> Bond distances in Å and bond angles in degrees.

<sup>b</sup>Core/valence correlation at the CCSD(T)/cc-pCVQZ level shortens the bond length by 0.0020 Å, resulting in an estimated CCSD(T)/aug-cc-pV5Z+CV value of 1.0975 Å.

<sup>c</sup>Constrained by symmetry to these angles. Linear for N<sub>3</sub> and N<sub>3</sub><sup>-</sup> and D<sub>5h</sub> for N<sub>5</sub><sup>-</sup>.

<sup>d</sup>The radical is cyclic with the symmetry unique atom N1 at the apex. N1 is bonded to N2 and N5 and N2 is bonded to N3 and N3 is bonded to N4. The bond distances are in the order: r(N1-N2) and r(N1-N5); r(N2-N3) and r(N4-N5); and r(N3-N4). The bond angles are in the order <N2N1N5; <N1N2N3 and <N1N5N4; and <N2N3N4 and <N5N4N3.

<sup>e</sup>The transition state for the anion decomposition is cyclic with the symmetry unique atom N1 at the apex. N1 is bonded to N2 and N5 and N2 is bonded to N3 and N3 is bonded to N4. The bond distances are in the order r(N1-N2) and r(N1-N5); r(N2-N3) and r(N4-N5); and r(N3-N4). The bond angles are in the order <N2N1N5; <N1N2N3 and <N1N5N4; and <N2N3N4 and <N5N4N3.

Table 2. Calculated Valence Correlated Harmonic Vibrational Frequencies (cm<sup>-1</sup>).

| Method                           | Mode Number | Mode Symmetry | Mode Description       | $\omega$          | Expt.                         |
|----------------------------------|-------------|---------------|------------------------|-------------------|-------------------------------|
| <b>N<sub>2</sub></b>             |             |               |                        |                   |                               |
| CCSD(T)/<br>aug-cc-pVDZ          | 1           | $\sigma_g$    | N <sub>2</sub> stretch | 2319              | 2331 <sup>a</sup><br>(2358.6) |
| CCSD(T)/<br>aug-cc-pVTZ          | 1           | $\sigma_g$    | N <sub>2</sub> stretch | 2340              |                               |
| CCSD(T)/<br>aug-cc-pVQZ          | 1           | $\sigma_g$    | N <sub>2</sub> stretch | 2354              |                               |
| CCSD(T)/<br>aug-cc-pV5Z          | 1           | $\sigma_g$    | N <sub>2</sub> stretch | 2359 <sup>b</sup> |                               |
| <b>N<sub>3</sub></b>             |             |               |                        |                   |                               |
| MP2/cc-pVTZ                      | 1           | $\pi$         | bend                   | 594               | 457 <sup>c</sup>              |
|                                  | 2           | $\sigma_g$    | symmetric stretch      | 1434              | 1320 <sup>c</sup>             |
|                                  | 3           | $\sigma_u$    | asymmetric stretch     | 1620              | 1645 <sup>c</sup>             |
| <b>N<sub>3</sub><sup>-</sup></b> |             |               |                        |                   |                               |
| CCSD(T)/<br>aug-cc-pVDZ          | 1           | $\pi$         | bend                   | 578               | 626 <sup>d</sup>              |
|                                  | 2           | $\sigma_g$    | symmetric stretch      | 1281              | 1335 <sup>e</sup>             |
|                                  | 3           | $\sigma_u$    | asymmetric stretch     | 1999              | 1986 <sup>f</sup>             |
| <b>N<sub>5</sub><sup>-</sup></b> |             |               |                        |                   |                               |
| CCSD(T)/aug-<br>cc-pVDZ          | 1           | $e_1'$        | NN stretch             | 1202              |                               |
|                                  | 2           | $a_1'$        | NN stretch             | 1141              |                               |
|                                  | 3           | $e_2'$        | NN Stretch             | 1078              |                               |
|                                  | 4           | $e_2'$        | bend                   | 1001              |                               |
|                                  | 5           | $e_2''$       | bend                   | 739               |                               |
| MP2/<br>aug-cc-pVDZ              | 1           | $e_1'$        | NN stretch             | 1143              |                               |
|                                  | 2           | $e_2'$        | NN stretch             | 1123              |                               |
|                                  | 3           | $a_1'$        | NN Stretch             | 1094              |                               |
|                                  | 4           | $e_2'$        | bend                   | 1039              |                               |
|                                  | 5           | $e_2''$       | bend                   | 740               |                               |
| <b>N<sub>5</sub><sup>+</sup></b> |             |               |                        |                   |                               |
| MP2/<br>aug-cc-pVDZ              | 1           | $b_2$         | NN str                 | 2260              | 2267 <sup>g</sup>             |
|                                  | 2           | $a_1$         | NN str                 | 2179              | 2206 <sup>g</sup>             |
|                                  | 3           | $b_2$         | NN str                 | 1199              | 1064 <sup>g</sup>             |
|                                  | 4           | $a_1$         | NN str                 | 881               | 870 <sup>g</sup>              |
|                                  | 5           | $a_1$         | bend                   | 669               | 671 <sup>g</sup>              |



|                        |   |                |   |      |                  |
|------------------------|---|----------------|---|------|------------------|
| MP2/<br>aug-cc-pVDZ    | 6 | b <sub>2</sub> | bend  | 431  | 414 <sup>g</sup> |
|                        | 7 | a <sub>2</sub> | out-of-plane<br>bend                                | 426  | 474 <sup>g</sup> |
|                        | 8 | b <sub>1</sub> | bend  | 374  | 421 <sup>g</sup> |
|                        | 9 | a <sub>1</sub> | bend  | 179  | 204 <sup>g</sup> |
|                        |   |                | N <sub>5</sub> <sup>-</sup> -TS                     |      |                  |
|                        | 1 | b <sub>2</sub> | NN stretch  | 1649 |                  |
|                        | 2 | a <sub>1</sub> | NN stretch  | 1572 |                  |
|                        | 3 | a <sub>1</sub> | NN stretch  | 1244 |                  |
|                        | 4 | a <sub>1</sub> | NNstretch   | 905  |                  |
|                        | 5 | b <sub>2</sub> | bend  | 848  |                  |
|                        | 6 | b <sub>1</sub> | bend  | 684  |                  |
|                        | 7 | a <sub>2</sub> | out-of-plane<br>bend                                | 591  |                  |
|                        | 8 | b <sub>2</sub> | bend  | 182  |                  |
|                        | 9 | a <sub>1</sub> | NN stretch  | 862i |                  |
|                        |   |                | N <sub>5</sub> (cyclic) <sup>2</sup> A <sub>1</sub> |      |                  |
| ZAPT2/6-<br>311+G(2df) | 1 | b <sub>2</sub> | NN stretch  | 1221 |                  |
|                        | 2 | a <sub>1</sub> | NN stretch  | 1147 |                  |
|                        | 3 | a <sub>1</sub> | NN stretch  | 1064 |                  |
|                        | 4 | b <sub>2</sub> | NN stretch  | 1033 |                  |
|                        | 5 | a <sub>1</sub> | NN stretch  | 1002 |                  |
|                        | 6 | a <sub>1</sub> | bend  | 843  |                  |
|                        | 7 | b <sub>2</sub> | bend  | 798  |                  |
|                        | 8 | a <sub>2</sub> | out-of-plane<br>bend                                | 729  |                  |
|                        | 9 | b <sub>1</sub> | bend  | 363  |                  |

<sup>a</sup> Ref. 33. Value in parentheses is the harmonic value.

<sup>b</sup> Core/valence correlation at the CCSD(T)/cc-pCVQZ level of theory increases the harmonic frequency by 9.2 cm<sup>-1</sup>, resulting in an estimated CCSD(T)/aug-cc-pV5Z+CV value of 2368 cm<sup>-1</sup>.

<sup>c</sup> Ref. 38

<sup>d</sup> Lamoureux, Dows, D.A.; *Spectrochim. Acta, Part A*, **1975**, 31, 1945. From N<sub>3</sub><sup>-</sup> in a KI lattice.

<sup>e</sup> References 40 and 41.

<sup>f</sup> Reference 35.

<sup>g</sup> Reference 2.



Table 3. Contributions to the total energy for  $N_x^m$  and relative energies.

| Contribution <sup>a</sup>                   | $N(^4S)$          | $N_2(^1\Sigma^+)$  | $N_3(^2\Pi)$ | $N_3(^1\Sigma^+)$ | $N_5(^1A_1')$ | $N_5^+(^1A_1)$ | $N_5^-TS(^1A_1)$<br>MP2 | $N_5^-TS(^1A_1)$<br>Ref. 7 geom |
|---|-------------------|--|--------------|-------------------|---------------|----------------|-------------------------|---------------------------------|
| aug-cc-pVDZ <sup>b</sup>                    | -54.486849        | -109.295320  | -163.770896  | -163.863661       | -273.142269   | -272.683885    | -273.101846             | -273.099657                     |
| aug-cc-pVTZ <sup>b</sup>                    | -54.516714        | -109.380845  | -163.900633  | -163.997758       | -273.360072   | -272.900359    | -273.317071             | -273.315909                     |
| aug-cc-pVQZ <sup>b</sup>                    | -54.525300        | -109.407243  | -163.939895  | -164.038815       | -273.428772   | -272.965446    | -273.383465             | -273.382442                     |
| Est. CBS Eq 1 <sup>c</sup>                  | -54.530069        | -109.422126  | -163.961942  | -164.061926       | -273.467671   | -273.001946    | -273.420892             | -273.419928                     |
| $\Delta E_{elec}$ CBS Eq.<br>1 <sup>d</sup> | 227.15            | 233.26   |              | 296.00            | 512.87        | 220.63         | 483.52                  | 482.91                          |
| $\Delta E_{CV}$ <sup>e</sup>                | 0.65              | 1.03   |              | 1.22              | 1.66          | 1.80           |                         |                                 |
| $\Delta E_{SR}$ <sup>f</sup>                | -0.11             | -0.51  |              | -0.51             | -1.04         | -0.85          |                         |                                 |
| $\Delta E_{ZPE}$ <sup>g</sup>               | -3.35             | -5.54  |              | -6.53             | -13.12        | -12.27         | -10.96                  | -10.0                           |
| $\Sigma D_0$ <sup>h</sup>                   | 224.34            | 228.34 <sup>k</sup>  |              | 290.18            | 500.37        | 209.31         |                         |                                 |
| $\Delta H_f(0K)$ <sup>i</sup>               | 112.53            | 0.72   | 109.25       | 47.41             | 62.28         | 353.34         |                         |                                 |
| $\Delta H_f(0K)$ expt                       | 0.0 <sup>29</sup> | 99.7 $\pm$ 5 <sup>29</sup><br>112 $\pm$ 5 <sup>41,42</sup> |              | 48 $\pm$ 2        |               |                |                         |                                 |
| $\Delta H_f(298K)$ <sup>j</sup>             | 0.76              | 108.6  |              | 47.4              | 59.6          | 351.6          |                         |                                 |

<sup>a</sup> Total energies in Hartrees and energy differences in kcal/mol.<sup>b</sup> Valence electron only CCSD(T) total energy with the given basis set. Open shell systems were treated with the R/UCCSD(T) method.<sup>c</sup> Estimated frozen core, complete basis set energy obtained from Eq.(1) using the CCSD(T)/aug-cc-pVxZ (x = D, T, Q) energies. For the sake of comparison, the CBS dissociation energy of  $N_2$  with the aug-cc-pVTZ through aug-cc-pV5Z basis sets is 226.63 kcal/mol.

<sup>d</sup> Valence electron atomization energy from extrapolated total energies obtained with Eq. 1.

<sup>e</sup> Core/valence correction obtained from R/UCCSD(T)/cc-pCVTZ calculations.

<sup>f</sup> Scalar relativistic correction obtained from CISD/cc-pVTZ calculations.

<sup>g</sup> Zero point vibrational energy contribution.

<sup>h</sup>  $\Sigma D_0 = \Delta E_{\text{elec}} + \Delta E_{\text{CV}} + \Delta E_{\text{SR}} + \Delta E_{\text{SO}} + \Delta E_{\text{ZPE}}$ .

<sup>i</sup> Enthalpy of formation at 0K.

<sup>j</sup> Enthalpy of formation at 298K.

<sup>k</sup> Spin orbit correction of +0.10 kcal/mol for N<sub>3</sub>